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INTEROFFICE MEMORANDUM

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EVALUATION OF THE USE OF GRADE 120 SLAG CEMENT IN TANK CLOSURE GROUT VERSUS PERFORMANCE ASSESSMENT ASSUMPTIONS

Purpose

The purpose of this memo is to evaluate the proposed activity of using Grade 120 Slag in tank closure grout versus assumptions contained within the H-Area Tank Farm (HTF) Performance Assessment (PA) (SRR-CWDA-2010-00128) and the F-Area Tank Farm (FTF) PA (SRS-REG-2007-00002). Section 3.2.3.3 of the bulk fill grout procurement specification (C-SPP-F-00055, Revision 4) currently specifies that only Grade 100 Slag Cement may be used. While tank grout meeting the grout fill formulation specifications will inherently meet the Tank Farm PA assumptions, a deviation from the specification does not necessarily lead to the grout not meeting the PA assumptions.

Background

Performance Assessment Grout Assumptions

Residual contaminants will be stabilized by filling the storage tanks with grout after the removal of waste. Grout is composed primarily of cement, sand, water, fly ash, slag, silica fume, viscosity modifier and high range water reducer. The grout mix must be flowable, pumpable and self-leveling. Grout is commonly used to solidify and stabilize radioactive wastes and the technology is at a mature stage of development. Stabilization with grout maintains the tank structure and minimizes water infiltration over an extended period of time, thereby impeding the release of stabilized contaminants into the environment. [DOE/SRS-WD-2012-001, DOE/SRS-WD-2014-001]

Grout will be used to fill the entire volume of the Type I, II, III/IIIA and IV tanks. Operational closure activities will be carried out using reducing grout to minimize the mobility of certain redox sensitive contaminants after closure (e.g., Tc-99). The grout formula is alkaline because grout is a cement-based material that naturally has a high pH, which is compatible with the carbon steel tank liner. The tank fill grout will have high compressive strength and low permeability, enhancing its ability to limit the migration of contaminants after operational closure. [SRS-REG-2007-00002, SRR-CWDA-2010-00128]

Grout requirements consist of both mechanical and chemical properties. The mechanical requirements of the grout are adequate compressive strength to withstand the overburden load (i.e., stability) and provision of a physical barrier to discourage intruders. The grout chemical composition (i.e., slag content) is used as an input in the PA modeling, since the grout is initially assumed to be reducing and basic, and transitions to oxidized and more acidic over time as infiltrating water enters the tank and changes the chemical conditions. Previous grout studies evaluated the chemical and mechanical properties of grout for tank closure. [SRNL-STI-2011-00551, WSRC-STI-2007-00369]

Slag Cement in Tank Closure Grout

Blast furnace slag is a normal by-product of the iron and steel industry. The major components of slag are oxides of silicon, aluminum, calcium, and magnesium; minor components include compounds containing manganese, iron, and sulfur. The exact concentrations of elements vary slightly depending on the source materials and additives used in the steel/iron production. Typical compositional ranges for blast furnace slag produced in the United States and Canada are shown in Table 2. [SRNL-PSE-2007-00282] Testing of Cast Stone (a grout formulation similar to saltstone proposed for encapsulation of low activity waste at the Hanford Site) using various slag chemical compositions [Table 4-1, PNNL-22747] has shown that reducing capacity is relatively insensitive to the slag chemical composition [Table 3.1, PNNL-22977].

Table 2: Compositional range for U.S. and Canadian blast furnace slags [Slag Association, 2007, Slag Cement Association Web Site].

Chemical constituent (as oxides)*	Range of compositions (mass percent)
SiO_2	32 - 42
Al_2O_3	7 - 16
CaO	32 - 45
MgO	5 - 15
S	0.7 - 22
Fe_2O_3	0.1 - 1.5
MnO	0.2 - 1.0

* Except for sulfur which is present as sulfide dissolved in the silicate glass. [Table 1, SRNL-PSE-2007-00282]

Granulated slag hydrates slowly on contact with water, but is activated to form insoluble hydrates in the presence of alkaline solutions (e.g., calcium hydroxide or sodium hydroxide, calcium sulfate, sodium carbonate, and sodium sulfate). The granulated slag is finely ground and marketed as a partial substitute for cement. The particle size distribution and the surface area of blast furnace slag is in general finer than or similar to that of Portland cements. [WSRC-TR-2001-00359]

ASTM C989 / C989M-14, *Standard Specification for Slag Cement for Use in Concrete and Mortars*, provides for three strength grades of Granulated Blast Furnace (GBF) slag (see Table 3). The grades are based on a slag-activity index: Grade 80 (low activity), Grade 100 (moderate activity), and Grade 120 (high activity). The numbers in the grade designations roughly correspond to the relative compressive strength at 28 days that standard mortar cubes made with GBF slag (blended with an equal mass of Portland cement) achieve compared to the strength of a plain Portland cement mortar mixture, in accordance with ASTM C989. The three grades are classified according to their slag activity index which is average compressive strength of the slag-reference cement cubes (SP), divided by the average compressive strength of the reference cement cubes (P), multiplied by 100 - [*Slag Activity Index (%) = (SP/P) *100*].

Table 3: Slag Activity Index Requirements [ASTM C989].

Slag Activity Index (minimum %)	Average of Last Five Consecutive Samples	Minimum in an Individual Sample
28 day index		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110

The standard also describes the mixture proportions for each type of cube as well as noting a size requirement of residue left on a No. 325 sieve (45μm) to be 20% and that the air content in the slag mortar not be greater than 12%. The chemical limitations of the standard are that the sulfide sulfur contents cannot exceed 2.5%. [ASTM C989]

The slag grades are more important for construction purposes than for waste encapsulation for which strength requirements are usually minimal. The chemical properties of the slag are more important for waste applications. Since these are not addressed in the ASTM specification, the chemical properties required for stabilization of contaminants must be specified by the user and verified by testing. [WSRC-TR-2001-00359] Per the grout fill formulation specification (C-SPP-F-00055, Revision 4), tank closure grout contains 210 pounds of Grade 100 Slag Cement per cubic yard. The proposed activity being evaluated would allow either Grade 100 or Grade 120 Slag Cement to be used during waste tank grouting.

Grout Chemical Properties

The PA models assume that the chemical properties (e.g., reducing capacity) of the fill grout changes as a function of pore volume flushing [SRNL-STI-2012-00404]. Once enough water flows through the pore volumes of the grouted waste tank, these models assume that the fill grout chemical properties transition from reducing to oxidizing. Because the timing of these transitions is determined based on grout formulation, the grout components (e.g., slag quantity) were developed with specific chemistry impacts (e.g., extended reducing capacity) in mind. The slag grade in the grout (and associated physical properties) does not impact the chemical properties (e.g., slag quantity) and therefore would not affect the PA assumptions regarding grout chemical properties. As stated earlier, testing of Cast Stone has shown that reducing capacity is relatively insensitive to the slag chemical composition. Testing performed on grout using Grade 120 slag confirmed that reducing capacity was not correlated to the slag grade (VSL-15R3740-1). It should also be noted that while the PA waste release analyses assumed a nominal slag composition [Table 2, SRNL-STI-2012-00404] for modeling purposes, the modeling recognized that "small deviations from these nominal values on rates of grout degradation would be small relative to the effects of other uncertainties". [SRNL-STI-2012-00404]

Waste Tank Stability

The Tank Farm PAs state that "the entire tank is assumed to be filled with grout; therefore structural failure (i.e., collapse) is not considered." The PAs assume that the grout has adequate compressive strength (i.e., 2000 psi, per FTF Table 3.2-4 and HTF Table 3.2-9) to withstand the overburden load on the tank at closure. The grout specification change does not impact the overall functionality of the grout material with regards to tank stability, as evidenced by the grout still being required to achieve a compressive strength of 2000 psi at 28 days. Testing performed on grout using Grade 120 slag has an average 28 day compressive strength of 2180 psi, which exceeds the 2000 psi compressive strength assumed in the PAs (SDDR #13182).

Tank Flow Modeling

The tank grout minimizes the flow of water from the tank top to the contamination zone at the bottom of the tank. The PA describes the assumed grout material properties (FTF PA Section 4.2.3.2.3 and HTF PA Section 4.2.2.2.4). The properties assumed in the modeling were selected from the testing described in WSRC-STI-2007-00369 and SRNL-STI-2011-00551. The grout formula was developed to meet the assumed material properties, with conformance to the grout formulation validated through adherence to the grout specification requirements. Allowing the use of Grade 120 slag in tank closure grout while not relaxing the other grout specification testing and performance requirements (e.g., flowability, weight of grout ingredients such as cement, sand, water, fly ash, slag, etc.,) will not impact the grout material overall functionality with regards to flow, since the grout permeability will not be impacted by the change in slag grade.

Conclusion

Use of Grade 120 Slag during Tank Farm waste tank closure is consistent with the inputs and assumptions contained within the Tank Farm PAs, and could be carried out in compliance with the Performance Objectives detailed within the PAs, assuming other grout performance and testing requirements are met.

References

ASTM C989 / C989M-14, *Standard Specification for Slag Cement for Use in Concrete and Mortars,* ASTM International, West Conshohocken, PA, www.astm.org.

C-SPP-F-00055, Rev. 4, *Furnishing and Delivery of Tank Closure Grout*, Savannah River Site, Aiken, SC, December 2012.

DOE/SRS-WD-2012-001, Basis for Section 3116 Determination for Closure of F-Tank Farm at the Savannah River Site, Savannah River Site, Aiken, SC, March 12, 2012.

DOE/SRS-WD-2014-001, Rev.0, *Basis for Section 3116 Determination for Closure of H-Tank Farm at the Savannah River Site,* Savannah River Site, Aiken, SC, December 2014.

PNNL-22747/SRNL-STI-2013-00465, Rev. 0, Westsik, J.H. Jr., et al., *Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests*, Pacific Northwest National Laboratory, Richland, Washington, September 2013.

PNNL-22977/EMSP-RPT-015, Um, W., et al., *Characterization of Technetium Speciation in Cast Stone*, Pacific Northwest National Laboratory, Richland, Washington, November 2013.

SDDR #13182, *Slag Cement not Meeting ASTM C989*, Grade 100, Savannah River Site, Aiken, SC, June 2015.

SRNL-PSE-2007-00282, Langton, C. A., *Functional Performance Requirements for Components in the Saltstone Premix*, Savannah River Site, Aiken, SC, December 2007.

SRNL-STI-2011-00551, Langton, C. A., and Stefanko. D. B., Rev. 1, *Tanks 18 and 19-F Structural Flowable Grout Fill Material Evaluation and Recommendations*, Savannah River Site, Aiken, SC, April 2013.

SRNL-STI-2012-00404, Denham, M., and Millings, M. R., *Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer During Post-Closure Aging of High-Level Waste Tanks*, Savannah River Site, Aiken, SC, August 2012.

SRR-CWDA-2010-00128, Rev. 1, *Performance Assessment for the H-Tank Farm at the Savannah River Site,* Savannah River Site, November 2012.

SRS-REG-2007-00002, Performance Assessment for the F-Tank Farm at the Savannah River Site, Savannah River Site, Rev. 1, March 31, 2010.

VSL-15R3740-1, Gong, W. A., et al., *Investigation of Alternate Grout Granulated Blast Furnace Slag for the Saltstone Facility*, Vitreous State Laboratory, Washington, DC, August 2015.

WSRC-STI-2007-00369, Rev. 0, Dixon, K., and Phifer, M., *Hydraulic and Physical Properties of Tank Grouts and Base Mat Surrogate Concrete for FTF Closure*, Savannah River Site, Aiken, SC, October 2007.

WSRC-TR-2001-00359, Rev. 0, Langton, C. A., et al., *State of the Art Report on High-Level Waste Tank Closure*, Savannah River Site, Aiken, SC, July 2001.

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